

UNCLASSIFIED

AD NUMBER

AD506894

CLASSIFICATION CHANGES

TO: unclassified

FROM: confidential

LIMITATION CHANGES

TO:

Approved for public release, distribution unlimited

FROM:

Distribution authorized to U.S. Gov't. agencies and their contractors; Specific Authority; 01 Mar 2001. Other requests shall be referred to Army Missile Command, ATTN: AMSMI-RK, Redstone Arsenal, AL 35898.

AUTHORITY

Jan 1982, Group-4, DoDD 5200.10; E-mail, 13 Mar 2001.

THIS PAGE IS UNCLASSIFIED

CONFIDENTIAL

COPY

A. D.

Technical Report S-242

**SYNTHESIS OF HTPB AND CTPB PREPOLYMERS BY
ANIONIC AND FREE-RADICAL POLYMERIZATION (U)**

by

Samuel F. Reed, Jr.

January 1970

**U. S. ARMY MISSILE COMMAND
REDSTONE ARSENAL, ALABAMA 35809**

Contract DAAH01-69-C-0772

**ROHM AND HAAS COMPANY
REDSTONE RESEARCH LABORATORIES
HUNTSVILLE, ALABAMA 35807**

This document contains information affecting the national defense of the United States within the meaning of the Espionage Laws, Title 18, U.S.C., Sections 793 and 794. The transmission or the revelation of its contents in any manner to an unauthorized person is prohibited by law.

**DDC
RECEIVED
FEB 9 1970
RECEIVED
D**

**DISTRIBUTION LIMITED
SEE INSIDE FRONT COVER**

CONFIDENTIAL

AD506894-6

AD506894

DISTRIBUTION LIMITATION

Initial distribution of this report has been made in accordance with contractual agreements and approved supplements received from our Contracting Officer. In addition to security requirements which apply to this document and must be met, each transmittal outside the agencies of the U. S. Government must have prior approval of the U. S. Army Missile Command, Redstone Arsenal, Alabama, ATTN: AMSMI-RK.

DISCLAIMER

The findings in this report are not to be construed as an Official Department of the Army position unless so designated by other authorized documents.

DISPOSITION INSTRUCTIONS

When this report is no longer needed, Department of the Army organizations will destroy it in accordance with the procedures given in AR 380-5. Navy and Air Force elements will destroy it in accordance with applicable directions. Department of Defense contractors will destroy the report according to the requirements of the Industrial Security Manual for Safeguarding Classified Information. All others will return the report to:

Department of Army
Headquarters, U. S. Army Missile Command
Redstone Arsenal, Alabama 35809
ATTN: AMSMI-IYC

GROUP 4
Downgraded at 3 year intervals;
declassified after 12 years

CONFIDENTIAL

January 1970

Technical Report S-242

**SYNTHESIS OF HTPB AND CTPB PREPOLYMERS BY
ANIONIC AND FREE-RADICAL POLYMERIZATION (U)**

by

Samuel F. Reed, Jr.

STATEMENT OF CLASSIFICATION

In addition to security requirements which apply to this document and must be met, dissemination outside the agencies of the U.S. Government must have prior approval of "AMSMI-RK"

**U. S. ARMY MISSILE COMMAND
Redstone Arsenal, Alabama 35809**

Contract DAAH01-69-C-0772

Distribution Limited

**DOWNGRADED AT 3 YEAR INTERVALS;
DECLASSIFIED AFTER 12 YEARS
EXPIRATION DATE 0000-10**

ROHM AND HAAS COMPANY

REDSTONE RESEARCH LABORATORIES

HUNTSVILLE, ALABAMA 35807

CONFIDENTIAL

Prior technical reports issued under Contract DAAH01-69-C-0772

S-191
S-193
S-199
S-204
S-207
S-209
S-211
S-217
S-220
S-221
S-223
S-225
S-227
S-230
S-231
S-232
S-235
S-236
S-238
S-240
S-241

CONFIDENTIAL

FOREWORD

The work described in this report was performed under Contract DAAH01-69-C-0772 for exploratory development of propellants for missiles and rockets under the technical cognizance of the Solid Propellant Chemistry Branch, Army Propulsion Laboratory and Center, Research and Engineering Directorate, U. S. Army Missile Command.

This report discusses the synthesis and characterization of hydroxyl- and carboxyl-terminated polybutadiene polymers. These polymers are of interest as binders for solid propellants having wide temperature limits. Preliminary studies on the anionic polymerization of butadiene were reported in Technical Report S-185 and studies on the free radical polymerization of dienes were reported in Technical Report S-196.

Special acknowledgement is made to Mr. R. D. Strahm and Dr. K. E. Johnson of these Laboratories for their contributions to this program. The technical assistance of Mrs. Alice Glover and Mr. J. O. Woods is appreciated.

ABSTRACT

This report describes the synthesis and characterization of polybutadienes and polyisoprenes possessing hydroxyl and/or carboxyl functionality. Polymer formation was accomplished through anionic or free radical initiated reactions. Characterization of the materials involved analyses for molecular weight, molecular weight distribution, microstructure, end-group content, and solution viscosity. The objectives of the program were to scale up the anionic polymerization of butadiene to produce a superior HTPB prepolymer, and to prepare by free radical techniques superior HTPB as well as hydroxyl- and carboxyl-terminated isoprene polymers for solid propellant binders.

Large-scale (100 gm) anionic polymerization of butadiene was carried out with two different dilithio initiators. A prepolymer (HTPB) exhibiting greater uniformity in properties was obtained with a commercial initiator than with an initiator prepared in-house. Functionality of the HTPB prepolymer ranged from 1.7 to 0.1 with average values near 1.0. In most respects these materials were comparable to similar commercial prepolymers. Preliminary gum stock and propellant development studies with the prepolymer confirmed their suitability as propellant binders.

Free radical polymerizations of butadiene and isoprene were carried out to give sufficient quantities of prepolymers for propellant development studies. Emphasis was focused on the preparation of HTPI and CTPI because the cis-1,4 form of polymer should lead to favorable low-temperature properties of these materials. Polymerizations carried out in various solvents demonstrated that the solvent has little effect on properties of the prepolymer. An important discovery was that the polymerization temperature plays an important part in determining the molecular weight distribution of the prepolymers formed in free radical polymerizations. Reactions leading to HTPB or HTPI conducted at 60°C or lower exhibited a polydispersity of 1.3 or less.

TABLE OF CONTENTS

	<u>Page</u>
Foreword	iii
Abstract	iv
Tables	vi
Section I. INTRODUCTION	1
Section II. CONCLUSIONS	5
1. Anionic Polymerization	5
2. Free Radical Polymerization	5
Section III. ANIONIC POLYMERIZATION	7
1. General Comments	7
2. Results and Discussion of Anionic Polymerizations	7
a. Polymerization	7
(1) Series I Prepolymers - Use of Dilithiopolyisoprene Initiator	8
(2) Series II Prepolymers - Use of DiLi-1 Initiator	10
b. Comparison of Prepolymer Properties	12
Section IV. FREE RADICAL POLYMERIZATION	15
1. General Comments	15
2. Results and Discussion of Free Radical Polymerization	15
a. Large-Scale Polymerization Reactions	16
b. Prepolymers for Methylation	18
c. Solvent Effects	21
d. Polymerization Temperature Effects	22
e. Further Characterization of HT-Polydienes	24
References	27

(U) TABLES

	<u>Page</u>
I. Tg of Some HT- and CT-Polydienes	3
II. HTPB Prepolymers. Experimental Data for Series I	9
III. Characterization Data for HTPB Prepolymers (Series I)	10
IV. HTPB Prepolymers. Experimental Data for Series II	11
V. Characterization Data for HTPB Prepolymers (Series II)	12
VI. Comparative Data for Series I and II Prepolymers	13
VII. Mechanical-Property Data on Propellants from Series I Prepolymers	14
VIII. Characterization Data for CTPB Prepolymers - Large-Scale Reactions	17
IX. Characterization Data for CTPB Prepolymers - Large-Scale Reactions	18
X. Characterization Data for HTPI Prepolymers - Large-Scale Reactions	19
XI. Characterization Data for CTPI Prepolymers - Large-Scale Reactions	20
XII. Characterization Data for CTPB Prepolymers - Prepared for Methylation	21
XIII. Characterization Data for CTPI Prepolymers - Prepared for Methylation	21
XIV. Characterization Data for CTPB Prepolymers - Solvent Effects	22
XV. Characterization Data for HTPI Prepolymers - Polymerization Temperature Effects	23
XVI. Characterization Data for HTPI Prepolymers - Polymerization Temperature Effects	23
XVII. Characterization Data for HTPB Prepolymers - Experimental Study	24

(Tables, continued)

Page

XVIII. Characterization Data for HTPI Prepolymers -
Experimental Study

25

XIX. Characterization Data for HTPC Prepolymers -
Experimental Study

25

CONFIDENTIAL

(THIS PAGE IS UNCLASSIFIED)

Section I. (U) INTRODUCTION

(U) Several polybutadienes, either hydroxyl-terminated (HTPB) or carboxyl-terminated (CTPB) are available for use as solid propellant binders. These include Thiokol's HC-434, Sinclair's Poly B-D® R-45M, and anionic polymers such as Phillip's Butarez® materials. For the reasons outlined below, none of the polydienes commercially available offers the ultimate in mechanical properties, particularly at low temperatures. This has prompted a program in the synthesis of functionally-terminated polydiene polymers for use as binders in solid propellant systems.

(U) Our preliminary studies of the anionic polymerization of butadiene established that an HTPB polymer with properties superior to those of Butarez HT could be prepared in small quantities. This experimental polymer had a high functionality (near 2.0), the desirable microstructure (up to 80% 1,4 polymerization), and a good molecular weight distribution (\bar{M}_w/\bar{M}_n were low); however some difficulty was encountered in preparing polymers of reproducible molecular weights.

(U) Section III of this report deals with the anionic polymerization of butadiene on a larger scale (100-gm runs) to see whether an HTPB polymer with superior properties could be produced in quantities sufficient for propellant development studies.

(U) Section IV of the report describes the results of free radical polymerization studies leading to the preparation of functionally-terminated polybutadienes and polyisoprenes. An improvement in low-temperature mechanical properties of solid propellants formulated with these binders, particularly the polyisoprenes, might be expected for the reasons that follow.

(U) The usual preparative techniques for polydienes give polymers composed of different structural forms, depending upon whether the diene monomer is incorporated into the chain in a 1,4-addition (cis-trans forms), 1,2- or 3,4-addition (vinyl forms), or a combination of these additions. Structural forms of the polydiene are commonly referred to as the microstructure of the polymer. The relative proportion of each microstructural form in the polydiene is dependent upon the specific conditions of the polymerization and upon the specific diene monomer. The low temperature properties of the polydiene are

CONFIDENTIAL

highly dependent upon the microstructure of the polymer; the microstructure determines the glass transition temperature (Tg) of the polymer, and Tg defines the modulus and tensile properties of the polymer.

(U) A brief comparison of available polydiene binder materials has been attempted, using the glass transition temperature (Tg) to define the character of the polymer's low temperature properties. The Tg is a useful property for comparative purposes since it defines the lower temperature limits at which the polymer will be useful as an elastomeric material. Tg's of polymeric materials have also been shown to be related to other polymer properties: hardness, brittleness, flexibility, toughness, and tackiness. Assuming the polydiene to be a copolymer or terpolymer of differing microstructural forms (cis-1,4, trans-1,4, and vinyl), and the Tg of the polymer to reflect the concentration of each form, one may calculate the Tg of the polydiene using the equation:

$$\frac{1}{T_g} = \frac{W_A}{T_{gA}} + \frac{W_B}{T_{gB}} + \dots + \frac{W_N}{T_{gN}} \quad \underline{1}$$

in which W is the weight fraction of monomer A, B....N in the polymer and Tg_A, Tg_B, etc. are the Tg values of the homopolymers. Tg values are expressed in degrees Kelvin.

(U) Applying the Tg calculations to polydienes which are currently being used, to some prepared in this study, and to some hypothetical examples gave the results reported in Table I. HC-434 and R-45M are representative of a CTPB and a HTPB, respectively, prepared by a free-radical mechanism. Their calculated Tg values are -37° and -35°C, and are slightly higher than the value calculated (-44°C) for the Butarez HT polymer prepared by anionic initiation. This difference in Tg between the free radical and anionic formed polybutadienes is attributed to the higher cis-1,4 content of the latter.

(U) The major conclusion arising as a result of the Tg calculations is that functional group-containing polyisoprenes and polychloroprenes may offer certain advantages in low temperature properties over similar polybutadienes. It is true that an all cis-1,4-polybutadiene would exhibit superior low temperature properties, but a high cis-1,4 content is not likely to be realized through any known practical preparation technique for HTPB and CTPB polymers.

Table I. (U) Tg of Some HT- and CT-Polydienes

No.	Polydiene	Microstructural Form, Weight %			Tg	
		Cis _{1,4}	Trans _{1,4}	Vinyl _{1,2}	°K	°C
1	HC-434 ^a	18.2	57.2	24.6	235.1	-37.1
2	R-45M ^b	15.96	61.2	22.8	238.1	-34.9
3	Butarez HT ^c	25.2	43.6	31.1	228.8	-44.2
4	IH-CTPB ^{a, d}	17.4	59.5	22.8	237.0	-36.0
5	IH-HTPB ^c	31.5	48.1	20.5	220.3	-52.7
6	IH-CTPI ^{a, e}	78.6	-	23.4	212.3	-55.7
7	Polybutadiene ^f	20.0	50.0	30.0	233.6	-39.4
8	Polybutadiene ^f	30.0	50.0	20.0	221.7	-51.3
9	Polybutadiene ^f	75.0	0	25.0	218.3	-54.7
10	Polyisoprene ^{f, h}	85.0	0	15.0 ^g	210.5	-62.5

^a Polymers formed by free radical initiation, carboxyl-terminated.

^b Polymers formed by free radical initiation, hydroxyl-terminated.

^c Polymers formed by anionic initiation, hydroxyl-terminated.

^d An average microstructure content of CTPB formed in four reactions.

^e An average microstructure content of CTPI formed in four reactions.

IH-CTPB

In-house CTPB

IH-HTPB

In-house HTPB

IH-CTPI

In-house HT-polyisoprene

^f Hypothetical cases.

^g Polyisoprenes prepared by free radical polymerizations contain 75-80% of the isoprene in the cis-1,4 configuration.

^h The vinyl-1,2 and -3,4 configurations were combined and assumed to possess a Tg of 300°K.

CONFIDENTIAL

(THIS PAGE IS UNCLASSIFIED)

(U) Section IV of this report, then, deals with the synthesis, by free radical initiation, of diene polymers containing a high percentage of cis-1,4 microstructure.

CONFIDENTIAL

CONFIDENTIAL
(THIS PAGE IS UNCLASSIFIED)

Section II. (C) SUMMARY AND CONCLUSIONS (U)

1. (U) Anionic Polymerizations

(U) A total of 28 anionic polymerizations of butadienes was carried out; the polymers were hydroxyl-terminated via ethylene oxide. Both a dilithiopolyisoprene initiator, prepared in batches for each polymerization, and a commercial initiator, Lithium Corporation of America's DiLi-1, were used.

(U) The polymers prepared from the batch-type initiator varied considerably in their properties. Molecular weights (\bar{M}_n) ranged from about 14,000 to 3,700, intrinsic viscosities ranged from 0.12 to 1.4, polydispersity ranged from 1.3 to 2.6, and functionality varied from 0.11 to 1.72. Considerable variation in the microstructure of the polymers was noted.

(U) The polymers prepared from the DiLi-1 initiator had a higher degree of reproducibility. Molecular weights (\bar{M}_n) ranged from 4,100 to 7,800, the intrinsic viscosity range was 0.08 to 0.35, polydispersity varied from 1.13 to 1.62, and functionality, although poor, ranged from 0.14 to 1.61.

(U) In most of their properties, the anionic polymers were about equal to commercial polymers such as Butarez HT; they certainly were not superior to any commercial materials. Thus, the difficult experimental techniques of this polymerization method are of questionable utility on a large scale. No further scale-up studies are planned.

2. (C) Free Radical Polymerizations (U)

(U) The free radical polymerization of butadiene and isoprene was examined; 4,4'-azobis(4-cyanovaleric acid) (AMCV) and 2,2'-azobis(5-hydroxy-2-methylvaleronitrile) (AMHV) were used as initiators. Polymerization reactions were carried out on 100-gm scale with butadiene and isoprene; HTPB, CTPB, HTPI, and CTPI polymers were produced and characterized.

(U) A series of 9 polymerizations of butadiene with 3 mole % AMHV gave polymers relatively uniform in character. The yields of polymer ranged from 54 to 76%, the molecular weight values ranged from 2,600 to 4,300, and functionality values varied

CONFIDENTIAL

from 2.16 to 3.18. The microstructure of the polymers changed little; the ratio of cis-1,4:trans-1,4:vinyl was about 16:61:23. When the initiator concentration was increased to 10 mole %, the molecular weight decreased to about 2,000.

(U) The properties of the CTPB polymers were similar to those of the HTPB polymers, except the molecular weights ranged from 3,100 to 8,500.

(C) Special attention was given to the HTPI and CTPI polymers. Their microstructure (75-80% cis-1,4) establishes these materials as promising candidates for solid propellant binders. The molecular weights (\bar{M}_n) of the HTPI polymers ranged from 2,300 to 3,300; functionality values of 1.35 to 2.53 were noted. The CTPI polymers had higher molecular weights (2,300 to 4,800) and higher functionality (1.61 to 3.30).

(U) Solvent effects on prepolymer properties appeared to be of little concern in the free radical initiated reactions. No significant change in property values could be detected when butadiene was polymerized in dioxane, acetonitrile, or dimethylformamide other than the expected higher molecular weight of products prepared in dioxane.

(U) A series of polymerizations carried out at varying temperatures produced a most unexpected result. It was found that butadiene or isoprene polymerizations carried out at 60°C or lower gave prepolymers with unusually low molecular weight distributions (< 1.3). In contrast, prepolymers prepared at 70°C or above displayed molecular weight distributions (> 1.4). This result represents the most significant discovery of the synthesis program because it eliminated one of the most serious drawbacks towards the application of free radically formed prepolymers as propellant binders. Heretofore, no prepolymers of this type possessing low polydispersities had been available for study. It would appear that free radically formed prepolymers are now competitive with those prepared by anionic initiation in terms of molecular weight distribution.

(U) Further studies are continuing in this program on temperature effects influencing polydiene properties. A complete evaluation of this discovery is important to the ultimate development of polydiene binder materials and to advance the current state of the art in this field.

Section III. (C) ANIONIC POLYMERIZATION (U)

1. (U) General Comments

(U) Basically, there are two general techniques for conducting an anionic polymerization in order to protect the reaction from oxygen and moisture. The first involves the use of an inert atmosphere (nitrogen, helium, argon) throughout the polymerization reactor; the second involves the use of an evacuated system. It was found that more consistent reproducibility in polymer properties was obtained when the polymerizations were conducted in an evacuated system. Consequently, the results described in this report were obtained from vacuum-line experiments. A rather detailed description of vacuum-line techniques suitable for anionic polymerizations has been reported by Fetters (1)¹.

(U) There are usually several steps involved in the anionic polymerization method. Those are: (a) equipment and reagent preparation, (b) initiator preparation, (c) diene polymerization, (d) termination, (e) hydrolysis of the lithium salt, and (f) polymer isolation. A detailed description of each step in the polymerization process and the methods for characterizing the prepolymers have been given in a previous report (2).

2. (U) Results and Discussion

a. (U) Polymerization

(U) The major objective of this program was to investigate the anionic polymerization of butadiene and the preparation of HTPB binder materials on a scale sufficient to supply the prepolymer for propellant evaluation studies. The reactions were carried out on a 100-gram scale. Specific objectives were to determine the reproducibility of the prepolymer properties and the suitability of the prepolymer as a propellant binder material.

¹ Numbers in parentheses refer to references at the end of the report.

CONFIDENTIAL
(THIS PAGE IS UNCLASSIFIED)

(U) Following the general procedure discussed earlier in this report, a total of 28 polymerization reactions were performed, the products isolated, and characterized. In the first series of 15 reactions, each reaction was initiated with a dilithiopolyisoprene solution prepared (1) individually for the specific reaction. The initiator used in the second series of 13 reactions was a commercial material (DiLi-1) purchased from the Lithium Corporation of America.

(U) DiLi-1 is a dilithium-isoprene oligomer mixture in a benzene-dimethyl ether solution (4). The weight percent composition of the solution is 11% oligomers, 6-7% dimethyl ether, and 82% benzene. The oligomer mixture consists of 75 to 90 mole % dilithium-diisoprene, 7 to 22 mole % dilithium-triisoprene, and 2 to 3 mole % dilithium-tetraisoprene. The solution is approximately 1.15N in active base and contains 5 mole % or less of a monofunctional dimer fraction. In many ways this initiator solution is similar to that prepared in-house (2).

(1) (U) Series I Prepolymers - Use of Dilithiopolyisoprene Initiator

(U) The experimental data for the first series of 15 reactions using the initiator prepared in-house are shown in Table II. In all instances, the polymerization was terminated by reacting the active polymer with ethylene oxide over a period of several days. At the point of introducing the ethylene oxide, a gel was obtained in all but one reaction, i. e., 97B. Methods of hydrolysis and prepolymer isolation have been described previously (2). The yields reported in Table II represent the yields of the purified products. Usually, 2 to 5% of the polymer was retained in the solvents (ether-methanol) used in the purification process.

(U) Characterization data obtained on the HTPB prepolymers are displayed in Table III. Table III contains molecular weight, end group, viscosity, microstructure, and gel permeation data. These data are indicative that the prepolymers vary considerably in their properties although prepared under very similar conditions. For instance, molecular weights (\bar{M}_n) ranged from approximately 14,000 to 3,700, intrinsic viscosities from 1.4 to 0.12, and polydispersity from 2.6 to 1.3. The lack of reproducibility in polymer properties may be attributed to the inability quantitatively to effect

CONFIDENTIAL
(THIS PAGE IS UNCLASSIFIED)

transfer of the initiator solution from the initiator preparatory flask to the polymerization flask (2). In addition, the reprecipitation procedure (purification) produces random variations in the samples and, hence, leads to less reproducibility in certain properties.

Table II. (U) HTPB Prepolymers. Experimental Data for Series I

No.	Initiator Preparation				Solvent (ml)	Solvent Removed (ml)	[B] (ml)	Time (hr)	Gel	Yield (%)
	[S] ^a	[Li]	[I]	[Ether] ^b						
90B	1.5	1.5	21.0	400	Tol-2000	825	155	21	Yes	91.7
93B	1.5	1.5	21.0	400	Tol-2000	800	158	19	Yes	77.2
94B ^c	1.5	1.5	21.0	400	Tol-2000	800	82	19	Yes	83.7
95B	1.5	1.5	21.0	400	Tol-2000	805	158	19	Yes	86.1
96B	1.5	1.5	21.0	400	Tol-2000	800	148	16	Yes	86.9
97B ^{d, f}	1.5	1.5	21.0	400	Tol-2000	810	150	20	No	67.6
98B ^f	1.5	1.5	21.0	400	Tol-2000	800	150	22	Yes	94.2
99B ^f	1.5	1.5	21.0	400	Tol-2000	800	150	16	Yes	96.4
100B	1.5	1.5	21.0	400	DEE ^b -1200	-	150	18	Yes	93.3
101B ^f	1.5	1.5	21.0	400	Tol-2000	850	160	18	Yes	92.8
102B ^{e, f}	2.25	1.5	21.0	400	Tol-2000	800	165	17	Yes	86.2
103B ^f	2.25	1.5	21.0	400	Tol-2000	600	140	18	Yes	92.1
104B ^f	2.25	1.5	21.0	400	Tol-2000	775	155	16	Yes	94.0
105B ^f	2.25	1.5	21.0	400	Tol-2000	800	145	18	Yes	82.2
106B ^f	3.0	1.5	21.0	400	Tol-2000	900	150	23	Yes	93.3

- ^a S = Stilbene
^b Diethyl Ether
^c Approximately 1/2 scale reaction
^d New ethylene oxide cylinder used
^e Vacuum system leaked overnight
^f Extra purification of solvent

CONFIDENTIAL
(THIS PAGE IS UNCLASSIFIED)

Table III. (U) Characterization Data for HTPB Prepolymers - Series I											
No.	\bar{M}_n	Weight % OH	Equivalent Weight OH	Functionality OH	Microstructure, %			G. P. C. Data			[η]
					Cis-1,4	Trans-1,4	Vinyl	\bar{A}_w	\bar{A}_n	PD	
90B	12800	0.18	9450	1.35	19.46	38.91	26.38				
93B	10000	0.11	15450	0.65	19.11	43.37	37.89	1191	919	1.30	0.860
94B	8100	0.22	7700	1.05	18.12	42.07	37.38	669	414	1.62	0.410
95B	7700	0.08	21500	0.36	17.72	35.50	40.69	1099	632	1.74	0.545
96B	5600	0.47	3625	1.54	21.09	43.50	30.16	446	304	1.46	0.293
97B	14000	0.05	34000	0.50	17.17	35.43	40.84	1880	731	2.57	1.400
98B	5400	0.37	4600	1.17	19.01	38.87	34.42	636	369	1.73	0.278
99B	5900	0.45	3775	1.56	20.20	40.88	28.22	406	258	1.58	0.275
100B	4000	0.63	2700	1.48	17.75	65.07	9.14	269	198	1.36	0.170
101B	10300	0.20	8500	1.21	20.68	44.30	30.17	755	460	1.64	0.420
102B	8200	0.36	4775	1.72	16.86	38.64	39.32	1046	414	2.52	0.325
103B	8500	0.24	7150	1.19	16.90	36.05	36.55	688	402	1.71	0.283
104B	5500	0.45	3715	1.46	18.47	40.24	33.07	489	309	1.59	0.190
105B	1400	0.13	13100	0.11	17.81	37.41	40.96	928	503	1.84	0.500
106B	3700	0.71	2400	1.54	20.58	43.69	28.84	233	175	1.33	0.120

(U) A relatively high degree of variation was observed in the microstructure of the prepolymers, particularly in the trans-1,4 and vinyl contents. The weight and number average Angstrom lengths of the polymers varied over a rather wide range, also. Functionality of the prepolymers ranged from 1.72 to 0.11 with a value of 1.13 being average. Several of the values were exceptionally low, and likely reflect errors associated with measurements of \bar{M}_n and end-group analysis rather than actual low functionality values. It is believed that the functionality of the prepolymers, in these instances, is higher than demonstrated by the analytical data. This is verified to some extent by the successful use of these prepolymers in propellant compositions, as reported later in this report.

(2) (U) Series II Prepolymers - Use of DiLi-1 Initiator

(U) The experimental data for the butadiene polymerizations employing the DiLi-1 initiator are shown in Table IV. Using DiLi-1 eliminated the initiator preparation step and simplified the entire procedure. A constant volume of the DiLi-1 solution (50 ml) was used in all reactions with solution transfer made by syringe. Gel formation was observed in only 5 reactions, although

CONFIDENTIAL

(THIS PAGE IS UNCLASSIFIED)

other reaction mixtures did give an observable increase in viscosity on addition of the ethylene oxide. Yields (87-99%) were very good and, generally, slightly higher than obtained in Series I reactions.

Table IV. (U) HTPB Prepolymers. Experimental Data for Series II						
No.	DiLi-1 (ml)	Solvent (ml)	[B] (ml)	Time (hr)	Gel	Yield
108B	50	Tol-2000	150	20	Yes	98.4
109B	50	Tol-2000	150	20	Yes	99.0
111B	50	Tol-2000	150	19	Yes	99.0
114B	50	Tol-2000	155	18	Yes	97.3
115B	50	Tol-1600	150	21	No	94.3
116B	50	Tol-1600	148	21	No	90.3
117B	50	Tol-1600	140	21	No	88.5
118B	50	Tol-1600	150	20	No	92.2
120B	50	Tol-1600	150	6	No	93.3
121B	50	Tol-1600	150	20	Yes	93.3
122B	50	Tol-1600	155	20	No	89.9
124B	50	Tol-1600	150	18	No	92.2
126B	50	Tol-1600	155	21	No	87.4

(U) Characterization data are shown in Table V. In general, there was a higher degree of reproducibility in property values of the polymers than observed in Series I polymers. For instance, the molecular weight (M_n) range was 4100 to 7800, the intrinsic viscosity range was 0.08 to 0.35, and polydispersity varied from 1.13 to 1.62. Other properties, including microstructure and G. P. C. data, were more uniform in character.

(U) Again there was a notable difference in the end-group analyses. The weight percent hydroxyl group content of the prepolymers ranged from a high of 0.49 to a low of 0.06. Consequently, these results affected the calculated equivalent weights and functionality values, both displaying a wide range of values. The average functionality was found to be 0.88.

CONFIDENTIAL

CONFIDENTIAL
(THIS PAGE IS UNCLASSIFIED)

Table V. (U) Characterization Data for ITPB Prepolymers -Series II											
No.	\bar{M}_n	Weight % OH	Equivalent Weight %	Functionality OH	Microstructure, %			G. P. C. Data			[η]
					Cis-1,4	Trans-1,4	Vinyl	\bar{A}_w	\bar{A}_n	PD	
108B	5600	0.49	3470	1.61	20.87	34.95	44.01	374	261	1.43	0.230
109B	4500	0.46	3700	1.22	21.95	33.79	43.37	323	244	1.32	0.229
111B	4900	0.46	3700	1.32	22.67	33.33	43.73	345	265	1.30	0.228
114B	6400	0.30	5650	1.13	22.73	31.10	46.74	371	235	1.58	0.253
115B	7800	0.13	13050	0.60	23.91	33.66	43.12	560	389	1.44	0.295
116B	6300	0.17	10000	0.63	22.94	32.91	43.88	409	299	1.37	0.255
117B	5100	0.19	8950	0.57	22.18	33.68	43.48	347	267	1.30	0.255
118B	5600	0.21	8100	0.69	21.30	34.63	43.46	618	381	1.62	0.335
120B	6100	0.29	5850	1.04	22.96	33.48	44.11	292	249	1.18	0.230
121B	5700	0.19	8950	0.64	22.78	32.95	43.52	593	442	1.34	0.355
122B	4100	0.06	28000	0.14	22.57	34.18	41.35	630	405	1.55	0.080
124B	4700	0.29	5850	0.80	21.11	35.66	42.76	295	226	1.30	0.135
126B	6100	0.28	6050	1.01	24.27	32.18	43.65	266	235	1.13	0.182

b. (C) Comparison of Prepolymer Properties (U)

(U) The characterization data on the prepolymers of Series I and II are compared with one another and with two types of Butarez HT prepolymers (Lots 612 and 5593). The property values reported in Table VI were obtained from measurements or calculations made in these Laboratories. It is immediately obvious that the uniformity in properties of the prepolymers prepared in Series II is significantly greater than for similar properties of the prepolymers in Series I. This is attributed to the more constant initiator concentration used in Series II reactions. Prepolymers in both series displayed moderately high to extremely low values for their functionality. Many of the low values may reflect errors inherent in the analytical determinations of molecular weight and end-group content of the prepolymers. In most respects, the prepolymers of Series I and II are the equal (average basis) of the commercial Butarez HT prepolymers.

CONFIDENTIAL

Table VI. (U) Comparative Data for Series I and II Prepolymers				
Property	Series I	Series II	Butarez HT (Lot-612)	Butarez HT (Lot-5593)
Gel Formation	14 of 15	5 of 13	-	-
Prepolymer Yields (%)	67-94	88-99	Good	Good
\bar{M}_n (V.P.O.)	3700-14000	4100-7800	4100	3900
Weight % OH	0.05-0.71	0.06-0.49	0.53	0.42
Equivalent Weight (OH)	2400-34000	3700-28000	3210	4050
Functionality	0.11-1.72 (1.13)	0.14-1.61 (0.88)	1.28	0.96
$[\eta]$	0.12-1.4	0.08-0.355	-	-
Microstructure Cis-1,4	~19-20	21-23	21	
(%) Trans-1,4	~38-42	42-44	42	
Vinyl	~34-36	32-34	30 ⁺	
\bar{A}_w	233-1880	266-630	341	357
\bar{A}_n	175-919	226-442	253	282
PD	1.30-2.57	1.18-1.62	1.35	1.27
Cure Behavior	O.K.	-	O.K.	O.K.

(C) Propellant compositions have been made successfully with prepolymers of Series I (98B, 99B, 102B, 103B, and 106B) and also with the Butarez HT prepolymers. The mechanical property data obtained on a number of compositions using Series I prepolymers are shown in Table VII. These data are preliminary, and it is pointed out that no attempt has yet been made to optimize the composition. It is apparent from these preliminary data that useful propellants can be obtained readily through the utilization of the prepolymers of Series I. Stress/strain data are given for an R-45M-based propellant, for comparative purposes. The propellant compositions were:

	Propellant Composition (%)	Propellant Composition (%)
Binder	9.91	9.60
Ammonium Perchlorate (cc/cc 70/30 blend)	70.64	70.64
Aluminum (H-10)	13.36	13.36
Emolein ^a + Curative	5.79	6.0
MT-4	0.3	0.4

^a Trademark of Emery Industries, Inc., Cincinnati, Ohio.

CONFIDENTIAL

CONFIDENTIAL

Table VII. (C) Mechanical-Property Data on Propellants from Series I Prepolymers (U)				
Prepolymer No.	TDI/Prepolymer (gm/gm)	Mechanical Properties		Stress/Strain at 140°F (psi/%)
		-40°F	77°F	
98B	0.419		82/62	
99B	0.480		73/52	
102B	0.414	217/84	64/49	57/96
Blend {	96B	0.33	No Cure	
	98B	0.43	133/45	22/76
	99B	0.53	178/59	51/73
	102B	0.63	297/47	73/26
	103B	0.83	No Cure	
106B	0.59		No Cure	
106B	0.79	473/12	180/12	144/12
106B	0.89	440/17	171/14	149/16
R-45M	-	205/41	113/37	88/33

(U) No propellants have been made using the prepolymers of Series II; however, these materials are known to cure satisfactorily with a TDI LHT-240 curative system in gumstocks, and their usefulness in propellants remains to be demonstrated.

CONFIDENTIAL

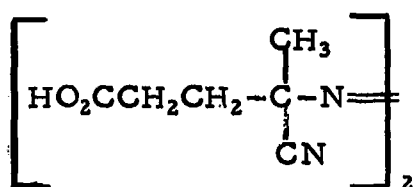
CONFIDENTIAL

(THIS PAGE IS UNCLASSIFIED)

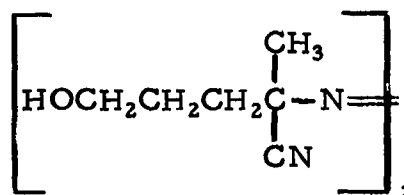
Section IV. (U) FREE RADICAL POLYMERIZATION

1. (U) General Comments

(U) The free radical polymerization of dienes with suitable functional group-containing azo initiators to yield HT- and CT-polydienes was a continuation of previous studies. The basic details of the experimental program were reported in an earlier report (3). It is important to point out that exclusive use was made of 4,4'-azo-bis(4-cyanovaleric acid) (AMCV) (I) from the Aldrich Chemical Company, or 4,4'-azo-bis(4-cyanopentanol) (AMHV) (II) prepared by the method of Bamford, et. al. (5) to initiate all free radical reactions.



I



II

2. (U) Results and Discussion of Free Radical Polymerization

(U) The major effect in the area of free radical polymerization was directed to the preparation of the prepolymers in sufficient quantities for propellant development studies. Prepolymers were prepared on a 100-gram scale for this purpose, and a concerted effort was directed to the preparation of HTPI and CTPI. It was of interest to ascertain the uniformity of properties of each type of prepolymers. Hence, a series of approximately 20 individual reactions for each type of prepolymer was completed and the prepolymer was characterized completely for comparative purposes. Subsequently, the prepolymers were blended according to type into a master batch for use in the propellant evaluation program.

(U) Associated polymerization studies were carried out on the preparation of CTPB and CTPI for use in methylation reactions leading to the development of an alternate method for obtaining the equivalent weight of the prepolymers. Details of this work will be reported elsewhere. The preparative work included the synthesis of a series of CTPB and CTPI prepolymers of varying molecular weights; characterization data on these two polymer series are described.

CONFIDENTIAL

CONFIDENTIAL
(THIS PAGE IS UNCLASSIFIED)

(U) A series of CTPB prepolymers was prepared in three different solvents, dioxane, acetonitrile, and dimethylformamide (DMF), to examine the effect of solvent on the prepolymer properties. Since the prepolymers separate from solution when the polymerizations are carried out in acetonitrile or dimethylformamide, it was thought that the prepolymers from these particular reactions could possibly possess a lower molecular weight distribution than those prepolymers formed in dioxane, which is an excellent polydiene solvent. All prepolymers were characterized in detail.

(U) In another related area of the synthetic work, a series of polymerizations was conducted at temperatures varying from 40° to 80°C. The influence of temperature on the properties of the prepolymers was unknown; however, it was thought that perhaps the microstructure of the prepolymer could be altered to some extent by the polymerization temperature. Both butadiene and isoprene were investigated in this study.

(U) The characterization data for HTPB, HTPI, and HTPC prepolymers reported (3) previously have been extended to include nitrogen, intrinsic viscosity, microstructure, and molecular weight distribution determinations. The data are presented for reference purposes.

a. (U) Large-Scale Polymerization Reactions

(U) Large-scale polymerization reactions (100 gm) were carried out with butadiene and isoprene to give HTPB, CTPB, HTPI, and CTPI prepolymers. A series of reactions was completed for each type of prepolymer. Detailed characterization of all prepolymers was accomplished by the usual means (Tables VIII, IX, X, and XI). After analysis, the individual prepolymers were blended, according to type, into master batches for later use in propellant formulation studies. Special effort was given to the preparative effort on the HTPI and CTPI prepolymers.

(U) Characterization data for the HTPB prepolymers are presented in Table VIII. The first 9 reactions were performed for comparative purposes. Using the high-low values for most measured properties, it was found that the prepolymers were relatively uniform in character. This was particularly evident through a comparison of the nitrogen content and the calculated equivalent weights. Molecular weight values ranged from 2600 to 4300 consequently, and produced a relatively wide range of functionality values,

CONFIDENTIAL
(THIS PAGE IS UNCLASSIFIED)

whether calculated using the hydroxyl or the nitrogen content. Less uniformity was observed in the intrinsic viscosities, where the range appeared to vary beyond the desired limits. Little change was observed in the microstructure of the prepolymers as one would have expected. The ratio (percent) of cis-1,4:trans-1,4:vinyl was in the range of 16:61:23.

Table VIII. (U) Characterization Data for HTPB Prepolymers - Large Scale Reactions [65°C - Dioxane-72 Hours-3 Mole % AMHV]												
FRB-No.	Yield %	\bar{M}_n	Weight % OH	% N	Equivalent Weight		Functionality		Microstructure, %			[η]
					OH	N	OH	N	Cis-1,4	Trans-1,4	Vinyl	
224	66.5	4300	1.50	1.20	1130	1165	3.81	3.69	15.96	61.15	22.90	0.109
225	76.5	2600	1.54	1.24	1100	1130	2.36	2.30	16.65	60.22	23.13	0.137
226	67.5	2800	1.61	1.23	1055	1140	2.65	2.46	17.04	59.16	23.80	0.098
227	59.0	2700	1.60	1.25	1060	1120	2.55	2.41	17.41	59.71	22.88	0.114
228	54.0	3600	1.42	1.18	1195	1185	3.01	3.04	← I →			0.132
236	63.0	2700	1.50	1.29	1130	1085	2.39	2.49	16.41	59.88	23.70	0.164
252	59.0	3600	1.17	1.09	1400	1285	2.57	2.80				0.138
263	59.0	2600	1.41	1.15	1205	1215	2.16	2.14	16.83	60.14	23.03	0.172
264	59.0	3400	1.41	1.11	1205	1255	2.82	2.71	17.07	59.94	22.99	0.180
325	63.0	1900	2.24	1.95	760	715	2.50	2.66	16.96	60.91	22.13	0.132
331	65.0	2000	2.24	1.81	760	750	2.63	2.67	15.04	62.04	22.93	0.106
332	-	1900	2.13	1.94	800	720	2.38	2.64	17.70	60.44	21.86	0.077

(U) The last three reactions (Table VIII) showed the effect of increasing the initiator (AMHV) concentration from 3 to 10 mole percent. The major effects were to lower the molecular weight from an average value of 2000 and to lower the related intrinsic viscosities accordingly. A low equivalent weight also resulted from this action. Little change was observed in functionalities or microstructure, although it was expected that the functionality values would increase.

(U) Similar data are reported in Table IX for the CTPB prepolymers. The molecular weights of these prepolymers were significantly higher than those of the HTPB. Values ranged from a high of 8500 to a low of 3100. Other properties appeared to be comparable. It was also noted that higher initiator (AMCV)

CONFIDENTIAL
(THIS PAGE IS UNCLASSIFIED)

concentrations (10 mole %) affected the prepolymers by lowering their molecular weight, equivalent weight, and intrinsic viscosity, as expected.

Table IX. (U) Characterization Data for CTPB Prepolymers - Large Scale Reactions [65°C -Dioxane-72 Hours-3 Mole % AMCV]												
FRB-No.	Yield %	\bar{M}_n	Weight %OH	%N	Equivalent Weight		Functionality		Microstructure, %			[η]
					CO ₂ H	N	CO ₂ H	N	Cis-1,4	Trans-1,4	Vinyl	
274	-	3100	3.30	1.32	1365	1055	2.27	2.94	17.95	58.14	23.91	0.154
275	67.5	3500	3.42	1.30	1315	1075	2.66	3.25				0.164
276	64.0	4400	3.11	1.21	1445	1155	3.04	3.81				0.140
277	65.0	3500	3.18	1.19	1415	1175	2.47	2.98				0.160
278	65.0	4800	3.35	1.15	1340	1220	3.58	3.93	16.66	59.65	23.69	0.184
279	75.0	4400	2.35	1.05	1915	1330	2.29	3.31	16.58	59.91	23.52	0.217
280	77.5	5300	2.81	1.05	1600	1330	3.31	3.99				0.231
281	72.5	6200	3.09	1.06	1455	1320	4.26	4.70				0.211
282	58.5	6200	3.24	1.13	1390	1245	4.46	4.98				0.170
283	61.5	8500	3.20	1.09	1405	1285	6.05	6.62				0.155
284	63.0	6400	3.32	1.14	1355	1230	4.72	5.20				0.176
285	58.0	5200	3.17	1.06	1420	1320	3.66	3.94				0.208
315	71.5	1100	6.21	2.59	725	540	1.52	2.04	19.37	56.60	24.03	0.138
326	74.0	1800	5.55	2.13	810	655	2.22	2.75	18.57	58.05	23.37	0.070
327	75.5	2000	5.78	2.19	780	640	2.56	3.12	19.42	57.28	21.12	0.070

(U) Data for the HTPI and CTPI prepolymers are reported in Tables X and XI. The prepolymer properties were similar in character to those observed for the polybutadienes. Obvious differences were noted in product yields. In most instances, lower yields were found for the polyisoprenes. Molecular weights of the HTPI prepolymers were lower than the CTPI.

b. (U) Prepolymers for Methylation

(U) A series of CTPB and CTPI prepolymers were prepared for methylation studies. It was of interest to obtain prepolymers of varying molecular weights for the methylation studies, since the methylated products were to be used in the development of a promising new method for equivalent weight determination.

CONFIDENTIAL
(THIS PAGE IS UNCLASSIFIED)

Characterization data for the prepolymers are displayed in Tables XII (CTPB) and XIII (CTPI). Initiator concentrations were varied from 0.5 to 5.0 mole percent to produce the prepolymers exhibiting molecular weights from about 2400 to 6500. The intrinsic viscosities of the prepolymers decreased in the expected order, and functionality values were usually in the range of 2 to 3. The molecular weight distribution (CTPI) appeared to decrease as the initiator concentration increased. This fact confirms the earlier reported results (3).

Table X. (U) Characterization Data for HTPI Prepolymers - Large Scale Reactions											
[65°C - Dioxane - 72 Hours - 3 Mole % AMHV]											
FRB-No.	\bar{M}_n	Weight % OH	% N	Equivalent Weight		Functionality		G. P. C. Data			[η]
				OH	N	OH	N	\bar{A}_w	\bar{A}_n	PD	
359	2900	1.44	1.28	1180	1095	2.46	2.65	284	170	1.67	0.121
360	2600	1.37	1.34	1240	1045	2.26	2.68	272	153	1.78	0.120
361	2200	1.04	1.14	1635	1225	1.35	1.80	256	147	1.75	
362	2900	1.04	1.10	1635	1205	1.77	2.41	274	163	1.68	
363	2300	1.04	1.21	1635	1155	1.41	1.99	242	145	1.67	
367	2800	1.54	1.49	1105	940	2.53	2.98	221	141	1.57	0.130
368	1500	1.33	1.12	1280	1250	1.17	1.20	224	132	1.70	0.122
369	2400	1.33	1.19	1280	1175	1.87	2.04	227	134	1.70	0.124
370	2400	1.39	1.23	1220	1140	1.97	2.11	233	132	1.76	0.124
371	2500	1.52	1.32	1120	1060	2.23	2.36	215	135	1.60	0.122
372	2700	1.34	1.30	1270	1075	2.13	2.51	239	142	1.68	0.115
373	2500	1.49	1.41	1140	995	2.19	2.51	230	136	1.69	0.138
	2800	1.47	1.39	1155	1005	2.42	2.79	217	127	1.70	0.143
375	2600	1.46	1.37	1165	1020	2.23	2.55	208	123	1.69	0.108
377	3000	1.16	1.16	1465	1205	2.05	2.49	248	154	1.60	0.101
378	3200	1.16	1.27	1465	1110	2.18	2.88	223	146	1.53	0.068
379	3300	0.96	1.17	1810	1195	1.82	2.76	206	139	1.49	0.077
380	2700	1.11	1.21	1530	1155	1.76	2.34	243	148	1.64	0.098
381	3300	1.12	1.17	1520	1195	2.30	2.93	222	149	1.49	0.117
382	2900	1.05	1.13	1620	1240	1.79	2.34	242	146	1.65	0.136
383	2700	1.11	1.15	1530	1215	1.76	2.22	229	133	1.72	0.060
384	2800	1.21	1.24	1405	1130	1.99	2.48	228	134	1.71	0.115

CONFIDENTIAL
(THIS PAGE IS UNCLASSIFIED)

Table XI. (U) Characterization Data for CTPI Prepolymers - Large Scale Reactions [65°C - Dioxane - 72 Hours - 3 Mole % AMCV]											
FRB-No.	\bar{M}_n	Weight % CO ₂ H	% N	Equivalent Weight		Functionality		G. P. C. Data			[η]
				CO ₂ H	N	CO ₂ H	N	\bar{A}_w	\bar{A}_n	PD	
286	4100	3.39	1.21	1325	1155	3.09	3.55	-	-	-	-
287	3700	3.18	1.14	1415	1230	2.61	3.01	253	146	1.74	-
288	4800	3.09	1.15	1455	1215	2.32	3.87	256	155	1.67	-
289	4800	3.09	1.21	1455	1155	3.30	4.16	231	140	1.65	-
290	2100	3.45	1.33	1305	1055	1.61	1.99	219	137	1.60	-
291	2400	3.51	1.31	1280	1070	1.88	2.24	229	139	1.64	-
292	2300	3.56	1.31	1265	1070	1.82	2.15	196	127	1.54	-
386	2600		1.47		955		2.72	166	114	1.45	0.095
387	2600		1.52		920		2.83	183	127	1.45	0.080
388	2800		1.39		1005		2.79				0.096
389	3800	2.55	1.09	1765	1285	2.15	2.96	241	142	1.69	0.115
390	3400	2.88	1.13	1565	1240	2.17	2.74	231	141	1.64	0.138
391	3700	3.14	1.11	1435	1255	2.58	2.95	233	142	1.64	0.130
392	3700	3.23	1.21	1390	1155	2.66	3.20	213	142	1.50	0.150
393	4100	3.46	1.20	1300	1165	3.15	3.52	211	143	1.48	0.118
394	4300	3.40	1.16	1320	1205	3.26	3.57	218	142	1.54	0.112
395	3700	3.28	1.17	1370	1195	2.70	3.10	234	143	1.64	0.120
396	4200	3.23	1.21	1390	1155	3.02	3.64	237	140	1.70	0.120
397	4200	3.28	1.15	1370	1215	3.07	3.46	223	141	1.58	0.120
398	3800							239	145	1.65	0.278
399	4000							256	158	1.62	0.284
401	4300	3.47	1.23	1295	1135	3.32	3.79	212	133	1.60	0.120
402	4300	3.42	1.13	1315	1240	3.04	3.23	229	143	1.60	0.121
403	3800	3.26	1.13	1380	1240	2.75	3.06	213	135	1.57	0.120
404	3000	2.45	1.21	1835	1155	1.63	2.60	213	133	1.60	0.119
405	3800	2.68	1.21	1680	1155	2.26	3.29	231	142	1.63	0.124
406	3400	3.19	1.28	1410	1095	2.41	3.11	233	140	1.67	0.132
407	3400	2.81	1.22	1600	1150	2.13	2.96	226	137	1.65	0.124
408	3900	2.95	1.20	1525	1165	2.56	3.35	245	148	1.66	0.116

CONFIDENTIAL
(THIS PAGE IS UNCLASSIFIED)

Table XII. (U) Characterization Data for CTPB Prepolymers - Prepared for Methylation [65°C - Dioxane - 72 Hours]												
FRB-No.	Mole % AMCV	\bar{M}_n	Weight % CO ₂ H	%N	Equivalent Weight		Functionality		Microstructure, %			[η]
					CO ₂ H	N	CO ₂ H	N	Cis-1,4	Trans-1,4	Vinyl	
297	0.5	6500	0.73	0.47	2325	2820	2.80	2.30				0.334
298	1.0	4600	0.96	0.47	1760	2820	2.61	1.63	16.04	60.96	23.00	0.313
299	2.0	5300	1.19	0.68	1430	2030	3.70	2.62	16.69	60.73	22.58	0.208
300	3.0	3800	1.85	1.09	920	1285	4.13	2.96	16.54	60.70	22.76	0.192

Table XIII. (U) Characterization Data for CTPI Prepolymers - Prepared for Methylation [65°C - Dioxane - 72 Hours]												
FP	Mole % AMCV	\bar{M}_n	Weight % CO ₂ H	%N	Equivalent Weight		Functionality		G. P. C. Data			[η]
					CO ₂ H	N	CO ₂ H	N	\bar{A}_w	\bar{A}_n	PD	
421	0.5	6300	1.27	0.59	3540	2375	1.78	2.65	239	142	1.62	0.237
422	1.0	5600	1.61	0.69	2790	2030	2.01	2.76	361	189	1.91	0.196
423	2.0	4300	2.33	0.99	1930	1415	2.22	3.04	258	156	1.65	0.110
424	3.0	3700	2.70	1.08	1670	1295	2.22	2.86	199	140	1.42	0.070
425	5.0	2400	3.73	1.89	1205	740	1.99	3.24	140	113	1.24	0.075

c. (U) Solvent Effects

(U) It had been noted earlier that when the dienes were polymerized in polar solvents such as acetonitrile or dimethylformamide (DMF), the polymer produced in the reaction separated from the solution to give a two-phase liquid system. The possible use of this phenomenon to aid in the free radical synthesis of polydienes exhibiting a low-molecular weight distribution was of interest to the polymer synthesis program. A series of polymerizations of butadiene were performed in dioxane, acetonitrile, and DMF to confirm experimentally that the product separating from solution (acetonitrile, DMF) was indeed one possessing a low polydispersity. The results of the characterization of the prepolymers (Table XIV) show that the polydispersity (PD) remains essentially unchanged regardless of the solvent and whether or not the product remains in solution or separate from solution during the reaction. Compare PD

CONFIDENTIAL
(THIS PAGE IS UNCLASSIFIED)

values of prepolymers prepared in the different solvents at similar initiator (AMCV) concentrations. Little change is noted. Again, the initiator concentration was an important factor in determining the PD of the prepolymers. The effects of solvent were very limited, with the most observable effect being its influence on molecular weight. Prepolymers prepared in dioxane (good solvent for polymer) had higher molecular weights and intrinsic viscosities than those prepared in acetonitrile (poor solvents for polymer). No change was noted in the prepolymer's microstructure.

Table XIV. (U) Characterization Data for CTPB Prepolymers - Solvent Effect [65°C - 72 Hours - AMCV]																
CT-No.	Yield %	Mole % AMCV	\bar{M}_n	Weight % CO ₂ H	%N	Equivalent Weight		Functionality		Microstructure, %			G. P. C. Data			[η]
						CO ₂ H	N	CO ₂ H	N	Cis-1,4	Trans-1,4	Vinyl	\bar{A}_w	\bar{A}_n	PD	
<u>DIOXANE</u>																
29	30	0.5	6500	1.26	0.53	3575	2640	1.82	2.46	← I →			823	415	1.98	0.420
3	59	3.0	3100	3.15	1.31	1430	1070	2.17	2.90	16.96	58.90	21.89	258	171	1.51	0.290
30	53	10.0	2200	4.70	1.78	960	785	2.29	2.80	19.38	57.72	22.90	143	125	1.15	0.125
<u>ACETONITRILE</u>																
139	8.5	0.5	3400	2.45	1.01	1835	1385	1.85	2.45	← I →			291	177	1.64	0.200
140	38	3.0	2600	3.53	1.31	1275	1070	2.04	2.43	16.82	59.68	23.50	198	141	1.41	0.148
141	43	5.0	2400	4.35	1.66	1035	845	2.32	2.84	18.58	57.87	23.55	151	113	1.33	0.108
142	46	10.0	1500	4.99	2.05	900	680	1.67	2.21	18.77	57.52	23.71	116	99	1.17	0.090
<u>DIMETHYLFORMAMIDE</u>																
98	26	0.5	6300	1.61	0.64	2795	2190	2.25	2.88	15.19	60.19	24.62	608	299	2.03	0.298
96	55	3.0	4800	2.84	1.09	1585	1285	3.03	3.74	13.66	62.50	23.84	249	171	1.46	0.200
97	30	5.0	2250	3.16	1.28	1425	1095	1.58	2.05	15.68	60.43	23.89	213	158	1.35	0.150

d. (U) Polymerization Temperature Effect

(U) An investigation of the effect of the polymerization temperature on the properties of the polydienes was carried out in reactions leading to the preparation of HTPB and HTPI prepolymers. Interest in this study centered on the possibility that the microstructure of the prepolymers could be altered by appropriate changes in reaction temperature. Polymerizations were conducted in duplicate at temperatures of 40°, 50°, 60°, 70°, and 80°C with butadiene and isoprene initiated with 3 mole % AMHV in dioxane. Tables XV and XVI contain the characterization data on these prepolymers.

CONFIDENTIAL
(THIS PAGE IS UNCLASSIFIED)

Table XV. (U) Characterization Data for HTPB Prepolymers - Polymerisation Temperature Effect [Dioxane - 72 Hours - 3 Mole % AMHV]																
FRB-No.	Temp., °C	Yield, %	\bar{M}_n	Weight %OH	%N	Equivalent Weight		Functionality		Microstructure, %			G. P. C. Data			[η]
						OH	N	OH	N	Cis-1,4	Trans-1,4	Vinyl	\bar{A}_w	\bar{A}_n	PD	
417	40	33	4300	0.95	0.86	1790	1625	2.40	2.65	-	-	-	293	218	1.34	0.150
418	40	24	4400	0.64	0.82	2655	1705	1.66	2.58	12.84	64.54	22.62	270	214	1.26	0.168
431	50	48	3600	1.15	0.93	1480	1505	2.43	2.39	15.19	61.70	23.12	211	171	1.24	0.134
432	50	50	3800	1.22	0.99	1395	1415	2.72	2.69	15.25	61.47	23.28	245	192	1.27	0.146
413	60	50	3300	1.29	1.12	1320	1295	2.50	2.55	16.45	61.10	22.45	192	158	1.21	0.118
414	60	50	3600	1.29	1.10	1320	1250	2.72	2.88	16.20	60.98	22.82	191	156	1.23	0.131
409	70	44	3700	0.90	0.87	1895	1610	1.95	2.30	17.32	59.64	23.04	367	187	1.96	0.216
410	70	43	3500	0.94	0.87	1810	1610	1.93	2.17	17.41	57.68	25.04	442	220	2.01	0.202
435	80	23	3300	1.24	0.99	1370	1415	2.41	2.33	17.84	59.03	23.13	326	173	1.89	0.213
436	80	35	3000	1.32	1.04	1285	1345	2.33	2.23	17.65	58.83	23.53	230	160	1.44	0.134

Table XVI. (U) Characterisation Data for HTPB Prepolymers - Polymerisation Temperature Effect [Dioxane - 72 Hours - 3 Mole % AMHV]																
FRB-No.	Temp., °C	Yield, %	\bar{M}_n	Weight %OH	% N	Equivalent Weight		Functionality		Microstructure, %			G. P. C. Data			[η]
						OH	N	OH	N	Cis-1,4	Vinyl-1,2	Vinyl-3,4	\bar{A}_w	\bar{A}_n	PD	
419	40	12	3900							-	-	-	225	178	1.27	
420	40	10	4300	0.64		2605		1.65		78.28	14.62	7.10	226	181	1.25	0.284
433	50	30	4100	1.26	1.02	1349	1370	3.03	2.99	77.40	15.05	7.55	175	146	1.20	0.072
434	50	30	3700	1.20	0.99	1415	1410	2.61	2.62	77.07	15.41	7.51	188	154	1.23	0.192
415	60	36	3700	1.25	1.10	1360	1270	2.72	2.91	77.67	14.87	7.44	173	136	1.27	0.138
416	60	29	3600	1.30	1.10	1305	1270	2.76	2.63	77.19	15.31	7.50	155	132	1.18	0.100
411	70	34	3400	1.06	1.07	1605	1285	2.12	2.65	77.63	14.73	7.63	254	149	1.70	0.066
412	70	36	3600	1.05	1.08	1620	1310	2.22	2.75	77.79	14.84	7.37	242	145	1.67	0.120
437	80	27	3600	1.22	1.08	1390	1295	2.59	2.78	75.62	17.00	7.38				0.149
438	80	35	2900	1.28	1.08	1325	1295	2.19	2.24	77.02	15.24	7.74	206	137	1.50	0.073

(U) The HTPB prepolymers prepared in duplicate runs at any given temperature displayed quite similar properties in most areas. No significant difference in the microstructure was apparent on comparison of the experimental data. The ratio of cis-1,4:trans-1,4:vinyl was about 16:61:23, as found previously for most reaction products prepared at 65°C. Other properties of these prepolymers were also similar (molecular weights, functionalities, etc.) except for the G. P. C. data.

CONFIDENTIAL

(THIS PAGE IS UNCLASSIFIED)

(U) It was immediately apparent that the prepolymers prepared at the lower temperatures possessed PD quite lower in value than those prepared at the higher temperatures. The natural break came in the temperature range between 60° and 70°C. All prepolymers formed in reactions at 60°C and below showed PD values of 1.3 or less, while those prepared at 70°C or above had PD values of 1.4 or greater. It is assumed that the normal reaction temperature of 65°C is on the high PD scale, since all reactions carried out at 65°C with 3 moles of AMHV gave a prepolymer with a PD value greater than 1.5.

(U) Similar behavior in the PD values was observed for the HTPI prepolymers (Table XVII) with the sharp break in high-low values coming between 60° and 70°C reactions. Other properties of the HTPI prepolymers were found similar to those reported for prepolymers prepared at 65°C.

Table XVII. (U) Characterization Data for HTPB Prepolymers - Experimental Study																	
[65°C - 3 Mole % AMHV]																	
FRB-No.	Time (Hr)	Solvent Volume (ml)	Yield (%)	\bar{M}_n	Weight % OH	% N	Equivalent Weight		Functionality		Microstructure (%)			G.P.C. Data			[η]
							OH	N	OH	N	Cis-1,4	Trans-1,4	Vinyl	\bar{A}_w	\bar{A}_n	PD	
DIOXANE																	
229	72	40	46.0	3100	1.35	1.08	1260	1300	2.46	2.38	18.04	59.55	23.40	300	189	1.59	0.200
230	72	20	51.5	3000	1.31	1.03	1300	1360	2.31	2.21	16.45	60.02	23.40	362	200	1.81	0.286
231	72	10	51.5	3700	1.33	0.98	1275	1430	2.90	2.59	15.70	61.72	22.59	407	220	1.85	0.296
TOLUENE																	
232	72	40	33.0	2500	1.37	1.05	1240	1330	2.02	1.80	← I →			451	206	2.19	0.260
233	72	20	35.0	3900	1.45	0.86	1170	1625	3.33	2.40	16.30	60.98	22.72	425	222	1.91	0.310
234	72	10	32.0	5000	1.19	0.75	1430	1870	3.50	2.67	15.59	61.55	22.86	559	276	2.03	0.350
TOLUENE																	
237	24	30	27.0	2400	1.23	1.07	1370	1305	1.75	1.84	16.10	60.33	23.57	251	186	1.35	0.184
238	48	30	36.0	2300	1.21	0.98	1405	1430	1.64	1.61	16.64	60.56	22.79	399	230	1.73	0.205
239	120	30	38.0	3500	1.03	0.90	1650	1555	2.12	2.25	17.09	60.89	22.02	436	228	1.91	0.434

e. (U) Further Characterization of HT-Polydienes

(U) The characterization of HT-polydienes has been extended to include nitrogen, intrinsic viscosity, micro-structure, and some molecular weight distribution analysis. The data (Tables XVII, XVIII, and XIX) are given for HTPB, HTPI, and HTPC, and are included for reference purposes.

CONFIDENTIAL
(THIS PAGE IS UNCLASSIFIED)

Table XVIII. (U) Characterization Data for HTPI Prepolymers - Experimental Study														
[65 °C - 3 Mole % AMHV]														
FRB-No.	Time (Hr)	Solvent Volume (ml)	Yield (%)	\bar{M}_n	Weight % OH	% N	Equivalent Weight		Functionality		Microstructure (%)			[η]
							OH	N	OH	N	Cis-1,4	Vinyl-1,2	Vinyl-3,4	
DIOXANE														
243	72	40	32.0	2400	1.16	1.08	1465	1295	1.64	1.85	76.81	15.73	7.46	0.125
244	72	20	36.0	2800	1.11	0.99	1530	1415	1.83	1.98	77.83	14.75	7.43	0.158
245	72	10	43.0	4500	1.07	0.97	1590	1495	2.83	3.01	77.44	15.16	7.40	0.153
TOLUENE														
248	72	40	26.0	3900	1.28	1.04	1325	1395	2.94	2.80	77.64	14.99	7.37	0.109
249	72	20	24.0	4500	1.11	0.96	1530	1460	2.94	3.08	77.64	15.08	7.28	0.120
250	72	10	28.0	2200	0.90	0.81	1890	1730	1.16	1.27	77.33	15.24	7.43	0.168
TOLUENE														
240	24	30	20.0	2700	1.21	1.00	1380	1400	1.96	1.93	78.84	14.34	7.23	0.125
241	48	30	27.0	2500	1.19	0.98	1405	1430	1.78	1.75	77.53	14.95	7.53	0.156
242	120	30	29.0	3700	0.96	0.86	1770	1625	2.09	2.28	77.98	14.64	7.38	0.209

Table XIX. (U) Characterization Data for HTPC Prepolymers - Experimental Study										
[65°C - 3 Mole % AMHV]										
FRB-No.	Time (Hr)	Solvent Volume (ml)	Yield (%)	\bar{M}_n	Weight % OH	% N	Equivalent Weight		Functionality	
							OH	N	OH	N
DIOXANE										
253	72	40	77.4	8400	0.66	0.50	2575	2800	3.26	3.00
270	72	30	87.6	4500	0.60	0.64	2885	2185	1.56	2.06
254	72	20	81.9	9700	0.59	0.48	2880	2920	3.37	3.32
255	72	10	84.2	10800	0.52	0.59	3270	2370	3.06	4.21
TOLUENE										
256	72	40	82.5	7500	0.60	0.55	2830	2590	2.65	2.89
257	72	20	81.9	6300	0.49	0.46	3470	3040	1.82	2.07
258	72	10	85.3	7500	0.42	0.44	3620	3180	2.07	2.36
DIOXANE										
260	24	30	86.4	5400	0.46	0.49	3695	2860	1.46	1.89
263	48	30	58.0	3900	0.59		2880		0.89	
262	72	30	85.3	3900	0.39	0.43	4360	3255	0.89	1.25
261	120	30	86.4	2800	0.48	0.60	3540	2380	0.79	1.18
TOLUENE										
265	24	30	84.8	5300	0.39	0.45	4360	3110	1.22	1.70
266	48	30	79.1	3000	0.41	0.45	4145	3110	0.72	0.96
267	72	30	88.7	5500	0.56	0.43	3030	3255	1.82	1.69
259	120	30	86.4	8600	0.35	0.47	4850	2980	1.77	2.89

CONFIDENTIAL

(THIS PAGE IS UNCLASSIFIED)

(U) REFERENCES

1. Fethers, L. J., J. Research National Bureau of Standards, A Physics and Chemistry, 70A, No. 5, 421 (1966).
2. Rohm and Haas Company, Huntsville, Alabama 35807, THE SYNTHESIS OF HTPB PREPOLYMERS BY ANIONIC POLYMERIZATION METHODS, S. F. Reed, Jr., November 1968, Technical Report S-185, U. S. Army Missile Command, Redstone Arsenal, Alabama 35809, Contracts DAAH01-67-C-0655 and DAAH01-68-C-0632 (Unclassified) AD 843 923.
3. Rohm and Haas Company, Huntsville, Alabama 35807, CONJUGATED DIENE POLYMERS FOR SOLID PROPELLANTS, S. F. Reed, Jr., January 1969, Technical Report S-196, U. S. Army Missile Command, Redstone Arsenal, Alabama 35809, Contract DAAH01-68-C-0632 (Confidential) AD 395 215 L.
4. Kamienski, C. W., Diesing, A. C., and Morrison, R. C. B., U. S. Patent, 3,388, 178, June 11, 1968.
5. Bamford, C. H., Jenkins, A. D., and Wayne, R. P., Trans. Faraday Soc., 56, 923 (1960).

CONFIDENTIAL

CONFIDENTIAL

(THIS PAGE IS UNCLASSIFIED)

DOCUMENT CONTROL DATA - R & D		
<small>(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)</small>		
1. ORIGINATING ACTIVITY (Corporate author) Rohm and Haas Company Redstone Research Laboratories Huntsville, Alabama 35807		2a. REPORT SECURITY CLASSIFICATION Confidential
		2b. GROUP 4
3. REPORT TITLE Synthesis of HTPB and CTPB Prepolymers by Anionic and Free-Radical Polymerization (U)		
4. DESCRIPTIVE NOTES (Type of report and inclusive dates)		
5. AUTHOR(S) (First name, middle initial, last name) Samuel F. Reed, Jr.		
6. REPORT DATE January 1970	7a. TOTAL NO. OF PAGES 27	7b. NO. OF REFS 5
8a. CONTRACT OR GRANT NO. DAAH01-69-C-0772	9a. ORIGINATOR'S REPORT NUMBER(S) Technical Report S-242	
8b. PROJECT NO.		
c.	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
d.		
10. DISTRIBUTION STATEMENT Initial distribution of this report has been made in accordance with contractual agreements. Qualified government agencies and contractors may obtain from Defense Documentation Center		
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Research and Engineering Directorate U. S. Army Missile Command Redstone Arsenal, Alabama 35809
13. ABSTRACT <p>This report describes the synthesis and characterization of polybutadienes and polyisoprenes possessing hydroxyl and/or carboxyl functionality. Polymer formation was accomplished through anionic or free radical initiated reactions. Characterization of the materials involved analyses for molecular weight, molecular weight distribution, microstructure, end-group content, and solution viscosity. The objectives of the program were to scale up the anionic polymerization of butadiene to produce a superior HTPB prepolymer, and to prepare by free radical techniques superior HTPB as well as hydroxyl- and carboxyl-terminated isoprene polymers for solid propellant binders.</p> <p>Large-scale (100 gm) anionic polymerization of butadiene was carried out with two different dilithio initiators. A prepolymer (HTPB) exhibiting greater uniformity in properties was obtained with a commercial initiator than with an initiator prepared in-house. Functionality of the HTPB prepolymer ranged from 1.7 to 0.1 with average values near 1.0. In most respects these materials were comparable to similar commercial prepolymers. Preliminary gum stock and propellant development studies with the prepolymer confirmed their suitability as propellant binders.</p> <p>Free radical polymerizations of butadiene and isoprene were carried out to give sufficient quantities of prepolymers for propellant development studies. Emphasis was focused on the preparation of HTPI and CTPI because the cis-1,4 form of</p>		

DD FORM 1473

REPLACES DD FORM 1473, 1 JAN 64, WHICH IS OBSOLETE FOR ARMY USE.

CONFIDENTIAL

CONFIDENTIAL
(THIS PAGE IS UNCLASSIFIED)

KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Polymerization						
Anionic						
Free Radical						
Functionally-terminated						
Dienes						
Polybutadiene						
Polyisoprene						
Polychloroprene						
Molecular weight						
Molecular weight distribution						
Viscosity						
Functionality						
Propellants						
Microstructure						
Synthesis						
Properties						
Initiators						
Abstract (Continued)						
<p>polymer should lead to favorable low-temperature properties of these materials. Polymerizations carried out in various solvents demonstrated that the solvent has little effect on properties of the prepolymer. An important discovery was that the polymerization temperature plays an important part in determining the molecular weight distribution of prepolymers formed in free radical polymerizations. Reactions leading to HTPB or HTPI conducted at 60°C or lower exhibited a polydispersity of 1.3 or less.</p>						

CONFIDENTIAL

Downing, Lawrence

From: Lyon, Mike RDEC [mike.lyon@redstone.army.mil]
Sent: Tuesday, March 13, 2001 11:01 AM
To: 'Downing, Lawrence'
Subject: RE: AD-506894, Question on Distribution Limitation

Mr. Downing,
The document to which you refer:

AD-506894 Jan 1970. Technical Report: S-242
"Synthesis of HTPB and CTPB Prepolymers by Anionic and Free-Radical
Polymerization"

may be declassified and redesignated (A) "approved
for public release; distribution unlimited"

J. Michael Lyon
Acting Director, Propulsion and Structures Directorate
US Army Aviation and Missile Command
Redstone Arsenal, AL 35898
(256) 876-3732

-----Original Message-----

From: Downing, Lawrence [mailto:ldowning@dtic.mil]
Sent: Tuesday, March 13, 2001 9:57 AM
To: 'mike.lyon@redstone.army.mil'
Cc: Kramer, Anna; Briggs, June
Subject: AD-506894, Question on Distribution Limitation

Mr. Lyon,

Request confirmation that AD-506894 is distribution/limitation (A) "approved
for public release; distribution unlimited".

Title: Synthesis of HTPB and CTPB Prepolymers by Anionic and Free-Radical
Polymerization

Date of Document: Jan 1970. Technical Report: S-242.

Lawrence D. Downing
DTIC-OCQ
703-767-0011
DSN 427-0011
ldowning@dtic.mil